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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : <b>A01G 5/06, A01N 3/02, A23B 7/144, A23L 3/3427</b>		A1	(11) International Publication Number: <b>WO 95/31093</b> (43) International Publication Date: 23 November 1995 (23.11.95)
(21) International Application Number: <b>PCT/AU95/00276</b>		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).	
(22) International Filing Date: <b>15 May 1995 (15.05.95)</b>		Published <i>With international search report.</i>	
(30) Priority Data: PM 5587 13 May 1994 (13.05.94) AU PM 6736 11 July 1994 (11.07.94) AU			
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(54) Title: CHEMICALLY-ACTIVE, ATMOSPHERE-MODIFYING DEVICE AND METHOD OF USE THEREOF			
(57) Abstract			
<p>An atmosphere modifying device including a substrate which has formed thereon a layer of chemical compound, said device being adapted to be placed in, on or near an object so that said chemical compound can make contact with said atmosphere around said object to thereby modify said atmosphere. The substrate may be a laminated label made from a polymer material onto which the chemical compound is printed or laminated. The chemical compound may be potassium permanganate or silver permanganate, and is adapted to control the atmospheric concentration of oxygen, water vapour, ethylene gas, or a combination of these substances. When the device is utilised in respect of being applied to fruit and vegetables and inside the containers or in plant boxes or punnets, the gases which deteriorate fruit and vegetables in a more rapid fashion than is normal, are in part or in whole, removed from the atmosphere. When the device is used in relation to the atmosphere on the surface of water in, for example, a vase, a bowl, a pond, an irrigation channel or a slow moving creek, the extraction of dangerous and harmful gases benefits the plants in the region and thus the other life around it. When the device also has nutrients involved, the plants surrounding the device will further benefit.</p>			

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**CHEMICALLY - ACTIVE, ATMOSPHERE - MODIFYING DEVICE AND METHOD OF USE THEREOF****FIELD OF THE INVENTION**

Present invention relates to the controlling of atmosphere around objects, in particular the surface of bodies of water such as is found in vases, bowls, ponds, irrigation channels, creeks, and around such objects as packaged foods, fruit and vegetables and horticultural products.

**BACKGROUND OF THE INVENTION**

Hitherto there has not been developed a cheap, practical and satisfactory method for the control of gases in the atmosphere around harvested fruit, vegetables and flowers. The main gases causing deterioration of such harvested fruit, vegetables and cut flowers is ethylene and oxygen. Ethylene has numerous physiological effects on horticultural products in storage, many of which are reduced by low temperatures and variable oxygen and carbon dioxide levels. Research has indicated that ethylene has a deterioration effect even under such conditions. Ethylene production by fruit and horticultural products is thought to be related to bruising, cutting, diseases and normal ripening processes. Some of the effects of ethylene are dramatic while others are subtle and may involve low levels of ethylene over long periods of time.

Ethylene is an initiator of fruit ripening or is a contributor to the ripening process.

Some of the methods used to control ethylene gas include the absorption by carbon; oxidation by ozone; destruction by UV radiation; catalytic oxidation; sachets of oxidising material packed with fruit and vegetables.

One prior art method is called Modified Atmosphere Packaging, which uses a specially treated plastic bag liner placed in the fruit or horticultural product container. The fruit or horticultural product is placed in the containers in layers and packed in the normal way. Close monitoring of the storage temperature during storage is required, so as to achieve lower levels of ethylene production, by a slowing down of the ripening process.

These methods of packaging do not give the fruit and horticultural products protection from the effects of ethylene gas after the boxes have been emptied at fruit stores, supermarkets or street stalls. From the time of being unpacked, the produce is effected by ethylene from bananas, apples and produce that generate ethylene in relatively large quantities. Ethylene gas is also generated from engines on fork lift trucks and motor vehicles.

Thus there has been a long felt need for an oxidising medium which travels with each piece of horticultural produce all the way to the moment of consumption.

Plastic bag liners are expensive, being in some cases equal to 10% of a growers return.

The quality of water can be decreased also by the atmosphere surrounding the water.

## 2.

**SUMMARY OF THE INVENTION**

The present invention provides an atmosphere modifying device including a substrate which has formed thereon a layer of chemical compound, said device being adapted to be placed in, on or near an object so that said chemical compound can make contact with said atmosphere around said object to thereby modify said atmosphere.

Preferably, the forming of the layer of chemical compound is by means of a printing process.

Preferably, the forming of said layer of chemical compound on said substrate is by a lamination process or a dipping process.

Preferably, the substrate is a laminated label, on which said chemical compound is printed or laminated.

Preferably, the substrate is a sticker or adhesive label.

Preferably said substrate is made of a polymer.

Preferably said device is made up of a polymer material or other suitable base to which a substrate is adhered, said substrate being printed with said chemical compound.

Preferably said chemical compound is mixed with a compatible ink for printing onto said substrate.

Preferably said compound is potassium permanganate ( $KMNO_4$ ).

Preferably said compound is silver permanganate.

Preferably 1.3 grams of said potassium permanganate or silver permanganate is first added to 100 millilitres of distilled water which is then dissolved and or mixed in 1 litre of a water based ink or varnish, or acrylic ink or varnish.

Preferably, said substrate is adapted to float on a liquid.

Preferably, said substrate is formed into coracle shape.

Preferably, said substrate is formed into a leaf shape.

Preferably, said coracle shape and said leaf shape are formed after forming said chemical compound on said substrate.

Alternatively, it is preferable that the coracle shape and the leaf shape are formed before forming said chemical compound on said substrate.

Alternatively, it is preferable that said device is formed by a sticker on which said chemical compound is deposited, said sticker being adhered to a floating object, a plant holding object, a fruit/vegetable holding object.

Preferably, if the forming process is by means of lamination, the chemical compound is located between two substrates with one or both of said substrates being adapted to allow said chemical compound to contact said atmosphere.

Preferably said two substrates are adapted to permit the flow of gases but not liquids.

## 3.

Alternatively preferable, one of said substrates is impervious to liquids and gasses and the other is impervious to liquid only.

Preferably, said chemical compound is adapted to remove ethylene gas from said atmosphere.

Preferably, substrate includes a nutrient means.

Preferably, said nutrient means is of a slow release type.

Preferably, said chemical compound is adapted to control oxygen, water vapour or ethylene gas or a combination of these.

Preferably, said chemical compound is of a chemical scavenger type.

Preferably, said chemical compound is adapted to release a specified gas as required.

Preferably said specified gas is carbon dioxide.

Preferably, said chemical compound is overlaid by an impervious covering.

Preferably, said impervious covering is adapted to be peeled, opened, moved or removed to allow said chemical compound to make contact with said atmosphere.

Preferably, said substrate is paper.

Preferably, said substrate is a polymer.

Preferably, said substrate is polystyrene.

Preferably, the nutrients consist of one or more of the following:

- Nitrogen in Nitrate form;
- Nitrogen in Ammonia form;
- Phosphorus in water soluble form;
- Phosphorus in Citrate soluble form;
- Potassium in Potassium Sulphate form;
- Sulphur in Sulphate form;
- Calcium in Calcium Phosphate form;
- Calcium Sulphate; or

having the following composition:

- Total nitrogen (N) 18% [Nitrogen in Nitrate form-7.5%; Nitrogen in Ammonia form-10.5%];
- Total Phosphorus (P) 4.8% [Phosphorus as a water soluble compound-4.3%; Phosphorus as citrate soluble-0.5%];
- Potassium (K) as Potassium Sulphate 9.1%;

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- Sulphur (S) as Sulphate 4%;
- Calcium (Ca) as Calcium Phosphate 9.6%.

Preferably, said nutrients are further coated with an organic resin coating.

Preferably, said organic resin coating is adapted to be dissolved by water or is adapted to break down over time.

Preferably, said chemical compound includes any one of the following or a combination of the following:

- Sulphur dioxide
- Ethanol;
- Metal Ions and salts of Propionic Acid;

Preferably said chemical compound is made up from an ink and an active ingredient used in a proportion of one part per thousand of ink up to one part per four thousand of ink.

The invention also provides a method of modifying an atmosphere around an object said method including the steps selecting an atmosphere modifying device as is mentioned above, for use with a predetermined object, applying said device to said object, or in or around said object or in the vicinity of said object, to modify in a localised fashion, the atmosphere in the vicinity of said object.

The advantage of the present invention is that when it is used in relation to the atmosphere on the surface of water in, for example, a vase, a bowl, a pond, an irrigation channel or a slow moving creek, the extraction of dangerous and harmful gases benefits the plants in the region and thus the other life around it. When the invention also has nutrients involved, the plants surrounding the device will further benefit.

When the device is utilised in respect of being applied to fruit and vegetables and inside the containers or in plant boxes or punnets, the gases which deteriorate fruit and vegetables in a more rapid fashion than is normal, are in part or in whole, removed from the atmosphere.

#### **DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

##### **Embodiment 1**

In a first embodiment, the invention is in the form of a floating plastic polystyrene object in the shape of a coracle, which has first been printed on with a chemical compound. Before the printing process, an atmosphere controlling chemical compound, specifically potassium permanganate, is pre-combined with an ink (as is described later), and is printed on one surface (or both) of a polystyrene substrate and the polystyrene is then pressed or formed into a coracle shaped object which will float.

When placed on a body of water, such a vase, a bowl, a pond, an irrigation channel, the potassium permanganate absorbs ethylene gas, and oxygen with which it combines to form carbon dioxide.

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#### **Embodiment 2**

A second embodiment is similar to embodiment 1, except that the layer of atmosphere controlling chemical compound, specifically potassium permanganate is added after the polystyrene has been formed into the appropriate shape. This done by a printing process, so that part or all of the shaped surfaces of the shaped object are coated.

#### **Embodiment 3**

A third embodiment is similar to embodiment 2 except that the device is formed into a flat plastic shaped form which is then dipped into a solution containing permanganate and ink in a ratio of 1 part potassium permanganate to 1000 parts water based ink.

#### **Embodiment 4**

The fourth embodiment is formed by adhering a sticker or adhesive label, which has an atmosphere controlling chemical compound printed thereon. The sticker or label is then stuck on to a polystyrene substrate in leaf shaped form.

Any of the above embodiments can then be used to float on the surface of water or if in the coracle shaped polystyrene can also be used as a box or punnet for berries, small fruits and plants. When the embodiments placed on or into water holding cut flowers, plants or aquatic plants, the atmosphere can be freed of ethylene gas by the atmosphere controlling chemicals.

#### **Embodiment 5**

A fifth embodiment includes embodiment a layer of atmosphere controlled chemical compound, specifically potassium permanganate or silver permanganate is laminated between two layers of material which are normally impervious to liquid. These layers control the rate or surface area of potassium permanganate and ink making contact with atmosphere by the gaps or apertures in the laminate or layer. This embodiment is utilised by attaching it directly to fruit or vegetables or to surfaces close to the fruit or vegetables. The laminate is preferably a hydrophobic membrane, such as is available under the trade mark VERSAPOR R

#### **Embodiment 6**

A sixth embodiment is similar to embodiment 5 except that instead of two previous layers, one is impervious to liquid and air such as a thin plastic substrate, to which a glue or adhesive is adhered to stick onto fruit or vegetables.

#### **Embodiment 7**

A seventh embodiment includes a substrate imprinted with an atmosphere controlling chemical, specifically being potassium permanganate or silver permanganate and ink, which is then covered by means of an atmosphere impervious layer such as a thin plastic layer. This cover is then peeled off or hinged open or otherwise moved or removed to thereby allow the atmosphere to make contact with the

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potassium permanganate or silver permanganate, when desired. The cover can be peeled off automatically by machine when the individual fruit or vegetables are labelled

**Embodiment 8**

Each of the embodiments 1 to 7 which utilise a polymer substrate can have that substrate replaced by a paper based substrate.

**Embodiment 9**

A ninth embodiment is identical to each of the previous embodiments which area adapted for use in except that a slow release nutrient is added to the substrate. In this embodiment the device, whilst withdrawing ethylene gas from the surface atmosphere, a further benefit of the slow release nutrient can be taken up by the plants from the water when the device is floated on water.

In each of the above embodiments the atmosphere controlling chemical is potassium permanganate and is combined in the following proportions. 1.3 grams of said potassium permanganate is first added to 100 millilitres of distilled water which is then dissolved and or mixed in 1 litre of a water based ink or varnish, or acrylic ink or acrylic varnish.

If it is desired the potassium permanganate can be substituted by silver permanganate in the same proportions as potassium permanganate. Both potassium permanganate and silver permanganate can be replaced by any one or a combination of any of the following:

- Sulphur Dioxide (a permitted fumigant for certain fruits to control mould growth);
- Ethanol;
- Metal Ions and Salts of Propionic Acid.

Potassium Permanganate is the preferred chemical for this invention. The proportions of Potassium Permanganate used to produce an atmosphere controlling chemical can be mixed in with ink in the proportions of one part potassium permanganate to one thousand parts of ink, down to one part potassium permanganate to one to four thousand parts of ink. The proportions will depend on the fruit or vegetables to which the devices or labels will be attached, the level of ethylene produced by the fruit or vegetable and other environmental conditions.

The selection of inks to be used together with the chemical compounds and the surfaces to be printed on can be selected by those skilled in the art according to the needs and other parameters in operation depending upon the situation being considered.

The nutrient means mentioned in embodiment 9 above, can be made up from any one or a combination of the following:

- Nitrogen in Nitrate form;
- Nitrogen in Ammonia form;
- Phosphorus in water soluble form;
- Phosphorus in Citrate soluble form;

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## 7.

- Potassium in Potassium Sulphate form;
- Sulphur in Sulphate form;
- Calcium in Calcium Phosphate form;
- Calcium Sulphate; or

having the following composition:

- Total nitrogen (N) 18% [Nitrogen in Nitrate form-7.5%; Nitrogen in Ammonia form-10.5%];
- Total Phosphorus (P) 4.8% [Phosphorus as a water soluble compound-4.3%; Phosphorus as citrate soluble-0.5%];
- Potassium (K) as Potassium Sulphate 9.1%;
- Sulphur (S) as Sulphate 4%;
- Calcium (Ca) as Calcium Phosphate 9.6%.

If a nutrient is used an organic resin coating can be used to place over the nutrients. In this case, the organic resin coating will deteriorate over time thus exposing the atmosphere controlling chemicals to atmosphere. Alternatively the coating when in contact with moisture laden air or when in contact with water dissolves thus exposing the potassium permanganate or silver permanganate.

Whilst the preferred substrates are polystyrene plastics, any floating objects such as composite materials or wood or other natural floating materials can be utilised.

Each of the embodiments described above have features which can be combined with other features of other embodiments, to produce an atmosphere modifying device which can be used in the same or in differing conditions or situations to those described.

In relation to the printing process, if the printing process is used to produce a readable message on the substrate, the colour of the atmosphere controlling chemical compound may need to be taken into account. For example, potassium permanganate when dissolved in water is generally of a pinkish colour and thus it will be necessary to take this colour into account if the atmosphere controlling chemical is to be printed with coloured inks, as background or as printed text. On the other hand, silver permanganate when in solution, is dark coloured and is particularly useful for dark coloured text. Generally sufficient atmosphere controlling effect can be achieved by using potassium permanganate or silver permanganate in the proportions described, in text printing only, on a label. A greater effect could also be produced if it was printed as background.

In respect of any of the embodiments which are suitable for attachment directly to fruit or vegetables, it is intended that the atmosphere controlling chemical compound does not come into direct contact with the fruit or vegetable. It is envisaged that the adhesive used to attach such a device will be safe to use on fruit and vegetables, and the types of these adhesives are well known in the appropriate industries.

## 8.

In respect of the embodiments that are adapted to float on water , function by acting on ethylene gas which may rise to the surface from decaying matter in the water. The decaying matter ma be flower stems or other plant material in the water which is decaying.

The above description and embodiments are also illustrative of the methods of use of the atmosphere modifying devices of the invention.

The advantages of the present invention when used in regards to fruit and vegetables and other horticultural products is that the atmosphere controlling compound will prolong the fresh appearance of fruit preserving the delicate nature of cut flowers by controlling the ripeness and aging process.

The adhesive backing on labels having atmosphere controlling chemical compound would depend on the surface of the packaged products to which the labels will be attached, for embodiment plastic polystyrene or various types of fruit and vegetables and horticultural products that they would be fixed to.

When the invention is utilised in respect of in water and other aquatic plants, flowers, plants and aquatic plants which are placed into or grown in the water may be freed of ethylene gas by the use of atmospheric controlled chemicals as used in the print medium or in the use of stickers or labels on which the atmosphere controlled chemicals have been placed in advance.

The foregoing describes some embodiments of the present invention and modifications by those skilled in the art can be made thereto without departing from the scope of the invention.

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## CLAIMS

1. An atmosphere modifying device including a substrate which has formed thereon a layer of chemical compound, said device being adapted to be placed in, on or near an object so that said chemical compound can make contact with said atmosphere around said object to thereby modify said atmosphere.
2. An atmosphere modifying device as claimed in claim 1, wherein the forming of the layer of chemical compound is by means of a printing process.
3. An atmosphere modifying device as claimed in claim 1, wherein the forming of said layer of chemical compound on said substrate is by a lamination process or a dipping process.
4. An atmosphere modifying device as claimed in any one of the preceding claims, wherein the substrate is a laminated label, on which said chemical compound is printed or laminated.
5. An atmosphere modifying device as claimed in any one of the preceding claims, wherein the substrate is a sticker or adhesive label.
6. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said substrate is made of a polymer on which said chemical compound is deposited.
7. An atmosphere modifying device as claimed in claim 1, wherein said device is made up of a polymer material or other suitable base to which a substrate is adhered, said substrate being printed with said chemical compound.
8. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said chemical compound is mixed with a compatible ink for printing onto said substrate.
9. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said chemical compound is potassium permanganate ( $KMNO_4$ ), or silver permanganate.
10. An atmosphere modifying device as claimed in claim 9, wherein 1.3 grams of said potassium permanganate is first added to 100 millilitres of distilled water which is then dissolved and or mixed in 1 litre of a water based ink or varnish, or acrylic ink or acrylic varnish.
11. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said substrate is adapted to float on a liquid.
12. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said substrate is formed into a coracle shape.
13. An atmosphere modifying device as claimed in any one of claims 1 to 11, wherein said substrate is formed into a leaf shape.
14. An atmosphere modifying device as claimed in any one of claims 12 or 13, wherein said coracle shape and said leaf shape are formed after forming said chemical compound on said substrate.

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15. An atmosphere modifying device as claimed in any one of claims 12 or 13, wherein the coracle shape and the leaf shape are formed before forming said chemical compound on said substrate.
16. An atmosphere modifying device as claimed in claim 1, wherein said device is formed by a sticker on which said chemical compound has been deposited, said sticker being adhered to a floating object, a plant holding object, a fruit or vegetable holding object.
17. An atmosphere modifying device as claimed in any one of the preceding claims, wherein if the forming process is by means of lamination, the chemical compound is located between two substrates with one or both of said substrates being adapted to allow said chemical compound to contact said atmosphere.
18. An atmosphere modifying device as claimed in claim 17, wherein said two substrates are adapted to permit the flow of gases but not liquids.
19. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said chemical compound is adapted to free ethylene gas from said atmosphere.
20. An atmosphere modifying device as claimed in any one of the preceding claims, said substrate includes a nutrient means.
21. An atmosphere modifying device as claimed in claims 20, wherein said nutrient means is of a slow release type.
22. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said chemical compound is adapted to control oxygen, water vapour or ethylene gas or a combination of these.
23. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said chemical compound is of a chemical scavenger type.
24. An atmosphere modifying device as claimed in claim 1, wherein said chemical compound is adapted to produce a predetermined gas, such as, for example, carbon dioxide.
25. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said chemical compound is overlaid by an impervious covering.
26. An atmosphere modifying device as claimed in claim 25, wherein said impervious covering is adapted to be peeled or opened or moved to allow said chemical compound to make contact with said atmosphere.
27. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said substrate is a polymer.
28. An atmosphere modifying device as claimed in any one of the preceding claims, wherein said substrate is polystyrene.

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29. An atmosphere modifying device as claimed in any one of claims 1 to 26, wherein said substrate is paper.

30. An atmosphere modifying device as claimed in any one of claims 20 or 21, wherein the nutrient has the following composition:

Total nitrogen (N)-18% [Nitrogen in Nitrate form-7.5%; Nitrogen in Ammonia form-10.5%];

Total Phosphorus (P)-4.8% [Phosphorus as a water soluble compound-4.3%; Phosphorus as citrate soluble-0.5%];

Potassium (K) as Potassium Sulphate-9.1%;

Sulphur (S) as Sulphate-4%; and

Calcium (Ca) as Calcium Phosphate-9.6%.

31. An atmosphere modifying device as claimed in any one of claims 20, 21 or 30, wherein said nutrients are further coated with an organic resin coating.

32. An atmosphere modifying device as claimed in claim 31, wherein said organic resin coating is adapted to be dissolved by water or is adapted to break down over time.

33. An atmosphere modifying device as claimed in any one of claims 1 to 8, or 13 to 32, wherein said chemical compound includes an active ingredient any one of the following or a combination of the following:

- Sulphur Dioxide;
- Ethanol;
- Metal Ions and salts of Propionic Acid;

34. An atmosphere modifying device as claimed in any one of claims 9, 10 or 33, wherein said chemical compound is made up from an ink and an active ingredient used in a proportion of one part active ingredient per one thousand parts of ink down to one part active ingredient per four thousand parts of ink.

35. An atmosphere modifying device as claimed in claim 17 or 18 wherein one of said substrates is impervious to liquids and gases and the other is impervious to liquid only.

36. A method of modifying an atmosphere around an object said method including the steps of selecting an atmosphere modifying device as is claimed in any one of the preceding claims, for use with a predetermined object, applying said device to said object, or in or around said object or in the vicinity of said object, to modify in a localised fashion, the atmosphere in the vicinity of said object.

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 95/00276

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int. Cl. <sup>6</sup> A01G 5/06; A01N 3/02; A23B 7/144; A23L 3/3427		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC : A01G 5/06; A01N 3/02; A23B 7/14, 7/144; A23L 3/3427, 3/3436, 3/3409		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU : IPC as above.		
Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) DERWENT : (IPC classes as above) and ETHYLENE		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	AU 63341/90 A (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 4 April 1991 pages 1-3, 5	1-8, 13, 16-19, 22, 23, 27-29, 34-36 9, 10, 20, 21
Y		
X, Y	EP 71533 A2 (ASSOCIATION POUR LA RECHERCHE ET LE DEVELOPPEMENT DE L'AMELIORATION DES PLANTES ET DES NOUVELLES TECHNOLOGIES; ARDANT) 9 February 1983 whole document	1, 3, 9, 10, 19, 22, 23, 36
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.		<input checked="" type="checkbox"/> See patent family annex.
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Date of the actual completion of the international search 18 July 1995		Date of mailing of the international search report 21 July 1995 (21. 07. 95)
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929		Authorized officer J. CARL Telephone No. (06) 2832543

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International application No.  
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
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International application No.

PCT/AU 95/00276

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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END OF ANNEX							